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REVIEW

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Pattern of parenchyma and canal resin composition in softwoods and hardwoods

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Abstract There is a general pattern of resin chemistry for parenchyma cells and secretory tissue. In sapwood the parenchyma resin is composed of fats, steryl esters, and occasionally waxes. Secretory tissue (most often resin canals) contains terpenes, terpenoids, and polyisoprenes. Other types of canal resin occur in a few hardwood families. The pattern is valid for softwoods and hardwoods. It has been defined from a comparison of available information on wood chemistry, wood anatomy, and the chemistry of oleoresin exudates from trees. This is a short overview with the most important references of two detailed reports.

Key words Wood resin · Parenchyma · Resin ducts · Terpenoids · Terpenes · Fats · Sterols

Introduction

In sapwood, resin is localized either in parenchyma cells or secretory tissue [resin canals, oil cells, and laticifers (latex tube cells)]. True wood resin has nonpolar, lipophilic (oleophilic)-extractable components with a dielectricity constant of <3.0. This definition distinguishes true resin from the other wood extractives, such as lignans, phenols, and carbohydrates. True wood resin can also be defined as four groups of chemical components.

Three of these groups in the sapwood are steryl esters, fats, and waxes. In heartwood these products hydrolyze into fatty acids, sterols, and fatty alcohols. These three groups of components in sapwood generally comprise the resin of parenchyma cells. The fourth group in true resin comprises terpenes and terpenoids. Usually they have a low molecular mass but occasionally occur as polymers. Terpenes are cyclic hydrocarbons. Terpenoids have one or more oxygen-containing functional groups. These components are biosynthesized mainly at the cambium from isoprene units by cyclization. In some hardwoods, isoprene in a linear mode polymerizes to polyisoprenes. Such polyisoprenes in the *cis* or *trans* form are included in the fourth group of resin components. In healthy sapwood this fourth group of resin components occurs in secretory tissue. Resin canals with their surrounding epithelial cells comprise the most common secretory tissue.

In hardwoods, there are two minor additional groups of canal resin. The components are slightly more polar, with a dielectric constant of <10. One group is the alkenyl diphenols and the other the phenoxy acid (poly)esters.

Parenchyma cells occur in all hardwoods and softwoods. In parenchyma resin the steryl esters appear to have a basic cell function. The amount of fats and waxes varies among species of any given genus. They appear to have a storage function. The overall resin content may comprise 10%–40% of the dry parenchyma cell weight. The epithelial cells around the canals contain all resin components.[1] They also synthesize canal resin usually made up of terpenes and terpenoids.

This general pattern is valid for the sapwood of both softwoods and hardwoods, as has been shown in great detail (E.L. Back, unpublished data). In heartwood the resin components become partly distributed throughout the tissue. Moreover, additional resin components are formed in many species, especially terpenyl alcohols. Thus the pattern is not valid for heartwood.

Oleoresin: function and collection

The oleoresin from canals usually has a viscosity suitable to flow and seal any wounds on tree surfaces. When homogeneous, it consists of a mixture of solid terpenoids dissolved in rather volatile terpenes. This gives a flow viscosity suitable for the ambient climate. The epithelial cells surrounding the resin canals exert on the canal resin a pressure of, for

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example, 10 atmospheres for suitable flow. The hydrophobic wound seal of canal resin is mainly mechanical. Some species (e.g., *Larix* and *Pseudotsuga*) also contain a significant amount of fungitoxic terpenyl alcohols in the canal resin.

As an alternative, canal resin might occur as a water suspension: a latex from which water evaporates. This is the case for the softwood genus *Auracaria*, which contains canals with resin acid dispersion in the bark. Another example is the polyisoprene latex in the laticifers of the inner bark of the rubber tree genus *Hevea*.

In the temperate climate zone, softwoods have generally been used for tapping oleoresin. Yet of 250 hardwood families, about 50 contain genera with resin canals (regular or traumatic canals) in the wood.[2] Many of them have been tapped for oleoresin. Examples are the myrrh oleoresin tapped from *Commiphora* species and the frankincense oleoresin tapped from *Boswellia* species. Both genera belong to the family Burseraceae. Among the seven softwood families, the family Pinaceae is the only one that contains some genera with regular resin canals in the wood. Most other softwood families have genera with regular resin canals in the bark. Bark oleoresin can be tapped as well. Among the hardwoods, about 15 families contain genera with oil cells in the wood,[3,4] 6 families contain genera with latex tube cells in the wood,[4] and other families contain latex tube cells in the bark. In some hardwood and softwood genera they occur locally as traumatic resin canals. These canals form in response to stress, wounding, or infection in a limited part of the wood tissue only.

Until around 1950 oleoresins were of great commercial use (e.g., for the production of paints and laquers and for the hydrophobation of paper). Lists of such oleoresin exudates exist for tree species and their chemistry, the latter unfortunately often based on early analytical techniques. Among Japanese hardwoods, resin canals occur in a *Rhus* species of the Anacardiaceae. They mainly contain a triple unsaturated alkenyldiphenol, urushiol. The "sweetgum", a *Liquidambar* species of the family Hamamelidaceae, contains a phenoxy acid polyester (cinnamic esters) in resin canals. Among tropical hardwoods of Southeast Asia, many genera with resin canals have been tapped for oleoresin for centuries. Among them is the family Dipterocarpaceae with the oleoresin damar. Because of its use as a stable lacquer on old Dutch paintings, modern analytical procedures have been used to explore its chemical composition. Its main components in addition to sesquiterpenes are the triterpenoids (some triterpenoic acids, some triterpenyl alcohols, triterpenyl ketones), which are different for different genera. In addition, damar contains about 30% of a unique polysesquiterpene with a molecular mass of 1000 to 10000 (see references in Back and Allen[1]). This polymer is difficult to disperse during alkaline pulping.

Diterpenoic resin acids make up the nonvolatile portion of the canal of softwoods and the African hardwood genus *Copaifera* of the Caesalpiniaceae subfamily of the Leguminosae. *Copaifera* oleoresin is called copal. Copal is also found in the fossil state like damar and the amber from pines around the Baltic and northern Atlantic.

Bridge from wood chemistry to wood anatomy

How can we establish and check the pattern of parenchymal and secretory resin chemistry? Three types of information must be compared (E.L. Back, unpublished observations).

1. Lists compiled by wood anatomists who have studied families and genera with the three types of secretory tissue: resin canals, oil cells, and laticifers in wood[2–6] and the bark[7–10]
2. Information on the chemical composition of various tree exudates (i.e., of collected oleoresins)[11–13]
3. Information compiled by wood chemists on the resin components of various trees, especially those containing terpenes and terpenoids or polyisoprenes in the wood[14,15]

For tree families or genera, where such data overlap and agree, the comparison leads to the following conclusions. Generally, the resin in canals and oil cells is composed of terpenes and terpenoids of the true resin components. Laticifers mainly contain polyisoprenes. They occasionally also contain terpenes and terpenoids. A few hardwoods contain two other types of lipophilic, aryl-based canal resin. One type is alkenyl-substituted diphenols, which occur in several genera of the Anacardiaceae. This resin occurs as a suspension (e.g., as Chinese, Japanese, or Burmese lacquer). It polymerizes easily at increased temperatures in a fashion similar to that of phenolic resins. During kraft pulping these and other reactive phenols can give rise to pitch specks. The other type of canal resin components comprises the (poly)esters of phenoxy acids.

For families or genera where the three types of information do not agree or information is incomplete, a detailed clarification is required (e.g., more experimental data). One problem is the occurrence of terpenoids as heartwood components in genera without secretory tissue.

Secretory tissue is absent in most hardwoods and softwoods. The resin in the sapwood is parenchyma resin exclusively and contains steryl esters, fats, and occasionally waxes. The parenchyma cells are the living cells of the sapwood and appear mainly in radial rays but also as axial lines. The resin occurs therein as droplets several microns in diameter.

There are hardwoods with gum (mucilage) canals, the gum of which contains polysaccharides or oligosaccharides mixed with minor amounts of protein. Trees with gum canals are listed separately by wood anatomists. Collected gums are also listed with their trees. One example is the gum arabic tapped from *Acacia* species of the Mimosaceae subfamily of the Leguminosae. The anatomical nature of mucilage canals is similar to that of the resin canals.

Heartwood

In heartwood, some of the existent sapwood resin components and often additional ones have become distributed throughout the tissue. Thus resin components occur as well within tracheids and especially in the vessels of hardwoods. Accordingly, the pattern presented is not valid for heartwood. Among the fungitoxic components formed during the transition to heartwood are terpenyl alcohols (especially sesquiterpenyl alcohols), which may occur together with phenols and lignans. When resin extracts are not clearly specified to healthy sapwood, the heartwood resin components can obscure the pattern. For example, many softwood genera without resin canals in the wood – and thus free from terpenoids in healthy sapwood – have terpenyl alcohols among their fungitoxic heartwood components. *Thuja* has highly fungi-resistant heartwood because of its thujaplicin content. The pleasent odor of juniper (*Juniperus*) originates from its heartwood sesquiterpenyl alcohol cedrol. Sugi (*Cryptomeria japonica*) among its heartwood components contains both sesquiterpenyl and diterpenyl alcohols. Some of these terpenyl alcohols also occur locally distributed in the sapwood tissue where fungi or bacteria have attacked.[16]

Teak (*Tectonia.grandis*) contains *cis*-polyisoprene rubber as a heartwood component. The resin tapped from *Guajacum* species in Central America actually comprises heartwood components in liquid form. This resin was collected for its historical use against syphilis. Clarification of such details is a necessary part of the detailed approach (E.L. Back, unpublished observations).

Exception: gasoline in the oleoresin of three pine species

It is common that nature develops a pattern with chemical components for certain functions. Yet there always is a chance of exceptions.

About 100 pine species appear naturally throughout the Northern hemisphere in which monoterpenes are the solvent for the resin acids in the canal resin of both wood and bark. The monoterpenes often occur as a mixture, and about 10 to 15 monoterpenes dominate. Yet, in three pines the solvent for the resin acids is totally or partly comprised of *n*-alkanes (i.e., linear saturated hydrocarbons). In *Pinus jeffreyi* wood about 85%–95% of the volatile substances is *n*-heptane, the remainder being other alkanes. Monoterpenes occur as well in the outermost annual rings. Monoterpenes occur also in the resin canals of the bark. In the leaves the volatile substances are only monoterpenes. The other two exceptional pines are *Pinus sabiniana* and *Pinus coulteri*. All three species grow in the mountainous area of southern California. The monoterpenes in the wood are biosynthesized from isoprene units at the cambium, whereas the *n*-heptane is biosynthesized from sucrose.[17]

As is evident from the terpene composition, mutations are common in pines at high altitudes due to ultraviolet radiation.[18] All three of the exceptional pines have three leaves in a bundle, an unusual combination among pines. Most of the pines contain two or five leaves in a bundle. The *Pinus jeffreyi*, with its *n*-heptane in the wood and bark, is most resistant to common bark beetles. Over millions of years a different, specific bark beetle has developed, called *Dendroctonus jeffreyi*. Its female has *n*-heptanol as a pheromone to attract the male beetle. *n*-Heptanol is formed also by oxidation of *n*-heptane.

Birch with polyisoprenols: an exception?

The family Betulaceae does not contain genera with secretory tissue. The sapwood resin is parenchyma resin. Yet in *Betula pendula*, the Scandinavian silver birch, 10%–20% of the resin extract is betulaprenol (i.e., isoprene alcohols mainly with seven or eight isoprene units).[19] The resin also contains a few percent of triterpenyl alcohols in the wood, mainly lupeol. These data on birch extractives do not specify sapwood and heartwood separately. Birch heartwood usually is uncolored and must be identified by microscopic inspection of the parenchyma cells and vessels. The heartwood and sapwood extract require separate investigation to establish the general pattern or any exceptions from it. Such data are not reported for *Betula pendula*.

Practical conclusions from these patterns

Conclusions refer both to wood properties and to pulping procedures. The attractive odor of monoterpenes in softwoods arises quickly, as canal resin is easily accessible in the wood. The negative odor of linear aldehydes originates late from oxidative scission of the unsaturated fatty acids in sapwood in the parenchyma cells. Thus, the emission of aldehydes proceeds with a slower diffusion process through the parenchyma cells. Moreover, the hydrophobation of freshly cut wood surfaces occurs with a different rate depending on whether canal resin is prevailing. Contact allergens in wood usually originate from canal resin, such as from resin acids and alkenyl diphenols. On wood or paper surfaces, resin acids and other terpenoids produce high sliding friction, whereas fatty acids produce low friction. The volumetric fraction of resin canals in the sapwood of a species can be calculated from the extracted terpene plus terpenoid fraction.

During the pulping operation the canal resin is easily accessible. For kraft pulping of softwoods, the resin acids are quickly dispersed and saponified. The diffusion of pulping liquor into the parenchyma cells takes time, as does the diffusion of parenchyma resin components out of these cells. Optimized removal of resin from unbleached pulps and during bleaching processes is mainly concerned with the parenchymal resin components. Some additional consequences of the pattern are discussed in a recent book.[1]

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